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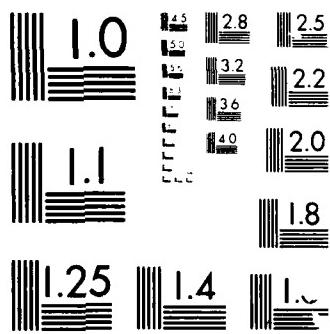
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Kinetic Titrations

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In liquid phase titrations endpoints are often determined by changes in absorption of light due to rapidly varying equilibrium concentrations around the endpoint of the titration. In gas phase titrations colors are due to emission of light due to chemiluminescent indicator reactions of active species. However, the titration reactions that produce or consume these active species are generally considered to proceed to completion in a time that is short compared to that in which observations are made on the reacting system.<sup>1</sup> Chemiluminescent gas-phase titrations are valued by kineticists for the simplicity with which they permit measurement of concentrations of atoms and free radicals and calibration of other methods of monitoring such concentrations. Identification of the endpoint in a gas-phase chemiluminescent titration may be by a change of color of the emitted light (N atoms<sup>2</sup>) or by the intensity of light reaching a constant (F atoms<sup>3,4</sup>), zero (Sn atoms<sup>5</sup>) or maximum level(O atoms<sup>6</sup>). The purpose of this report is to indicate an alternative type of gas-phase titration, in which a chemiluminescent reaction is used as both the titration and indicator reaction, and the endpoint of the titration is determined as the point of "maximum persistence" of chemiluminescence. It will be shown that defining the endpoint by this criterion can provide information concerning mechanism and kinetics of the chemiluminescent reaction, as well as its stoichiometry.

A simple explanation for the principle of maximum persistence is as follows: It is the nature of a second

order reaction that, if one of the reactants is present in great excess, the reaction will be pseudo-first order. As long as the reactants are not present in stoichiometric proportions, at some time during the time course of the reaction, the limiting reagent will be consumed to the point that pseudo-first order conditions for its decay will hold. The decay of concentration of the limiting reagent under pseudo-first order conditions is exponential, while that at the stoichiometric condition is second order and thus inversely proportional to time (at long time). Since exponential decay is more rapid than  $1/t$  decay, at long time the stoichiometric mixture will always decay more slowly than mixtures with any other proportion of reagents.

Although defining the endpoint of a titration reaction as the point of maximum persistence is not limited to reactions that are monitored by observing light emission, in practice the application of this definition is limited by a number of factors. The first requirement is that the reaction be monitored by a technique that measures a property nearly proportional to the instantaneous rate of reaction. Light emission by the product of a chemiluminescent reaction is such a property, if the emitter is lost (by radiation and quenching) on a time scale that is rapid compared to the characteristic time of the reaction. A second requirement is that the method by which reaction rate is monitored has sufficient sensitivity for measuring this rate at long times, when the rate has declined by several orders of magnitude from its initial value. The great sensitivity of photodetectors in the visible and ultraviolet region, together with the possibility of using these detectors in pulse counting modes will often satisfy this sensitivity requirement. In fact, in several cases ( $\text{F}_2 + \text{H}$  and  $\text{F} + \text{CH}_3\text{OH}$ ), we believe that we have identified



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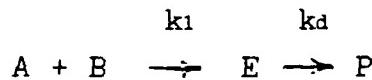
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endpoints visually by observing maximum persistence of luminescence.

Case I: titration in an elementary reaction

Consider a second order reaction between A and B to produce a light emitting product, E.



If  $a_0$  and  $b_0$  are the initial concentrations of A and B and  $x$  is the concentration of either A or B that is consumed, the kinetics of this equation are described by

$$1) \frac{dx}{dt} = k_1(a_0 - x)(b_0 - x).$$

This equation can be solved by the method of partial fractions<sup>7</sup> to give

$$2) \frac{1}{(b_0 - a_0)} \ln(\frac{a_0(b_0 - x)}{b_0(a_0 - x)}) = k_1 t,$$

which can be rearranged to

$$3) x = a_0(\exp y - 1)/(\exp y - g),$$

where  $g = a_0/b_0$  and  $y = (1-g)b_0 k_1 t$ .

Assuming that A and B are present at low concentration in an inert carrier, the decay of E (by radiation or quenching) will be first order in the concentration of E (with rate constant  $k_d$ ) and independent of that of A and B. The steady-state concentration of E will then be

$$4) E_{ss} = (k_1 a_0 b_0 / k_d) (1 - (\exp y - 1) / (\exp y - g)) * (1 - g(\exp y - 1) / (\exp y - g))$$

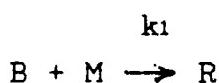
Alternatively,

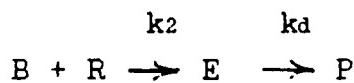
$$5) E_{ss} k_d / k_1 b_0^2 = g(1 - (\exp y - 1) / (\exp y - g)) * (1 - g(\exp y - 1) / (\exp y - g))$$

The right-hand side of equation (5), which is proportional to the emitted light intensity for a given initial amount of B, is plotted as a function of g in figure 1 for different values of  $b_0 k_1 t$  over the range 10-100. These curves have been normalized to the peak value at  $b_0 k_1 t = 10$ . The expression is undefined for  $g=1$ , but can be evaluated for values arbitrarily close to  $g=1$ . In these logarithmic plots, light intensity peaks very close to the stoichiometric ratio (within 0.4% at  $b_0 k_1 t = 10$ , much closer at larger  $b_0 k_1 t$ ). The peak is not very sharp at  $b_0 k_1 t = 10$ , but becomes increasingly sharp and reduced in intensity as  $b_0 k_1 t$  increases. Considering the logarithmic nature of the plot, the endpoint of the titration would be easily located at values of  $b_0 k_1 t > 30$ . Adjusting the concentration of A (or the flow of A in a flow reactor) to observe this sharply peaked light emission allows the endpoint of the titration of B with A to be accurately determined. At times shorter than those plotted in figure 1, the maximum shifts progressively to higher values of g. (When very little B is consumed, intensity is proportional to the concentration of A.) The variation of light intensity around the stoichiometric end point is determined by  $b_0 k_1 t$ . Thus for known  $b_0$  (determined by the endpoint of the titration) and  $t$  (determined by distance and flow velocity in a flow reactor),  $k_1$  may be determined by matching to the curves in figure 1, which are a very sensitive function of  $b_0 k_1 t$ .

#### Case II: titration in a series mechanism

Persistent luminescence may also be observed in reactions that proceed by a multistep mechanism. Analysis of such systems may permit stoichiometric, mechanistic and kinetic information to be obtained about these systems. For example, consider the simple two-step series mechanism,





The steady-state approximation for R,

$$6) \quad R = k_1 M / k_2 ,$$

holds when  $k_1 \ll k_2$ . If x is the concentration of B consumed, at steady state  $x/2$  is the concentration of M consumed, and the kinetics are described by

$$7) \quad dx/dt = 2k_1(b_0 - x)(m_0 - x/2),$$

which can be integrated by partial fractions to give

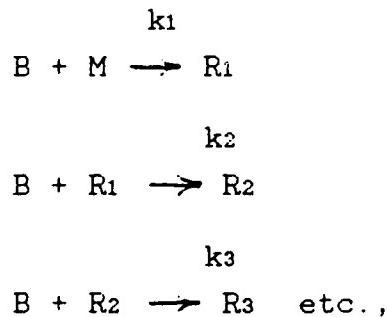
$$8) \quad 1/(b_0 - 2m_0) \ln(2m_0(b_0 - x)/b_0(2m_0 - x)) = k_1 t.$$

With the substitution of  $2m_0$  for  $a_0$ , this is clearly the same equation as (1). Plots of emission intensity vs.  $g'$ , where  $g' = 2m_0/b_0$ , for a two-step series mechanism at steady state are thus identical those shown in figure 1 for an elementary reaction. At sufficiently long times emission is sharply peaked at  $g' = 1$  ( $b_0 = 2m_0$ ), the equivalence point of the reaction. Variation around this point, in units of  $g'$ , is determined by  $b_0 k_1 t$ , where  $k_1$  is the rate constant of the rate-limiting reaction.

In order to test the importance of the steady-state requirement for sharply peaked emission at the endpoint, we have modeled, using the Gear algorithm, the two-step series mechanism under the condition  $k_1 = k_2$ , which clearly does not satisfy the steady-state condition. Results of this calculation (normalized to the value at the peak of the  $b_0 k_1 t = 10$  curve) are shown as crosses adjacent to the three curves in figure 1. Although there are small quantitative differences from the steady-state curves, the qualitative conclusion that light emission at long times is sharply peaked at the stoichiometric concentration ratio is still valid.

For the two-step mechanism, it is also possible to consider the limit  $k_1 \gg k_2$ . In this case the first reaction goes rapidly to completion, consuming  $m_0$  of B. Luminescence from the second reaction then peaks at its equivalence point, when a second  $m_0$  of B is consumed. Thus in this limit as well, light emission at long times is strongly peaked at the equivalence point of the overall reaction ( $b_0 = 2m_0$ ). However, variation of luminescence around the equivalence point is now determined by the value of  $k_2(b_0 - m_0)t$ , since reaction (2) is now rate limiting, and  $b_0 - m_0$  of B are available for this reaction. In this case,  $g = m_0/(b_0 - m_0)$  when using figure 1. Although we have not attempted a general proof, it appears that in the two-step series mechanism, long-time light emission will always peak at the endpoint of the reaction.

It is also possible to draw some conclusions regarding a general series mechanism, of the form



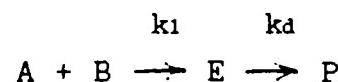
where any of the products,  $R_1$ ,  $R_2$ , etc., emit light. If the first reaction in this mechanism is rate limiting, intermediate Rs will be in steady-state and remain at low concentrations proportional to that of M. If there are n reactions in the series, n Bs will be consumed simultaneously for each A that reacts. The long time behavior will then follow equation (6) with  $g = nm_0/b_0$  on the curve determined by  $b_0 k_1 t$ . Note that since each R is

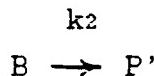
maintained in steady state with M, this conclusion holds regardless of which R is the luminescent product.

If the initial reaction is not rate limiting, the results depend upon whether the rate limiting reaction in the series comes before or after the production of the luminescent product. If the rate-limiting step comes before the production of the luminescent product, say after  $n'$  steps,  $n'm_0$  Bs will be rapidly consumed, and the initial M will be converted to  $Rn'$ . Subsequent Rs will then be in steady state with  $Rn'$  and will all be formed at maximum long-term rates when just an additional  $(n-n')m_0$  of B are available. Once again maximum long-term emission will occur at the overall equivalence point,  $b_0 = n'm_0$ . The variation of the emission around the endpoint will now be determined by the value of  $kn'+1(b_0-n'm_0)t$  and is in the variable  $(n-n')m_0/(b_0-n'm_0)$ . If, however, the rate-limiting step occurs after the formation of the luminescent intermediate, the buildup of the slowly reacting intermediate will result in pseudo-first order decay of B on the time scale of the reactions producing the luminescence. On the other hand, very little of the luminescent intermediate will remain on the time scale of the overall reaction. Thus, unless the rate-limiting step is very slow (In which case, it might not be appropriate to consider it in the stoichiometry of the reaction.), no persistent luminescence will be observed in this case. It thus appears that for any series mechanism, if persistent luminescence is observed, maximum persistence should occur at the stoichiometric equivalence point of the reaction.

### Case III: Parallel Mechanisms

One important parallel mechanism is,





This mechanism holds, for example, when during titration of active species B with titrant A, B is simultaneously lost by a wall reaction. Eliminating t from the differential equations for this system we obtain

$$9) \quad db/da = (k_1 a + k_2)/k_1 a,$$

which integrates to

$$10) \quad b = b_0 + (a - a_0) + k_2 (\ln a/a_0)/k_1$$

This gives

$$11) \quad da/dt = -k_1 a b = -k_1 a (b_0 + (a - a_0) + k_2 (\ln a/a_0)/k_1)$$

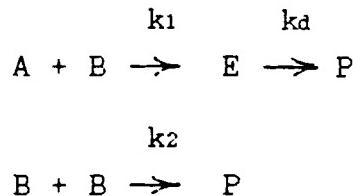
After integrating and substituting  $g = a_0/b_0$ ,  
 $x = a/a_0$  and  $r = k_2/k_1 a_0$ ,

$$12) \quad a_0 k_1 t = \int_x^1 dx' / (x' (g^{-1} + (x' - 1) + r \ln x')).$$

This equation has been numerically integrated, using Simpson's rule with as many as 150 intervals to achieve sufficient accuracy. If  $r$  is small enough, the results are extremely similar to those of case I. For example, for  $r = 10^{-3}$ , intensity variation as a function of  $g$  is indistinguishable from the curves in figure 1. However, for  $r = 10^{-2}$  the differences from figure 1 are substantial. Thus,  $r = 10^{-3}$  should be considered the upper limit in order to avoid appreciable deviation of the point of maximum persistence of luminescence from the stoichiometric endpoint of the titration. For atoms, very low wall recombination rate constants ( $k_w < 0.1 \text{ sec}^{-1}$ ) can usually be achieved with appropriately treated walls. Thus wall recombination will generally be negligible for rapid ( $k_1 > 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ ) bimolecular chemiluminescent reactions of atoms. (Assuming

atomic concentrations of the order of  $10^{14} \text{ cm}^{-3}$ , probably necessary to obtain sufficient intensity to observe long-time luminescence.) For termolecular chemiluminescent reactions, high concentrations of both atoms and third bodies will be necessary for wall loss to be negligible. Wall loss rate constants are usually  $> 1 \text{ sec}^{-1}$  for di- and polyatomic radicals. Thus care will be necessary to assure negligible wall loss for both bimolecular and termolecular chemiluminescent reactions. (Even though termolecular rate constants are generally considerably larger than for atoms.)

Another parallel mechanism of interest involves two competing second order reactions.



This mechanism would hold, for example, if an active species underwent homogeneous recombination simultaneously with being titrated. In this case,

$$13) \quad \frac{db}{da} = (k_1 a + k_2 b) / k_1 a$$

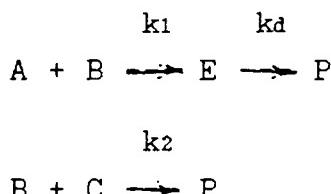
which becomes  $da/a = db/b$  if

$$14) \quad a/b = 1 - k_2/k_1.$$

Since this ratio depends only on the rate constants and not on concentrations (or time), if the initial ratio of concentrations is set to (14), it will remain at this value during the reaction. With A and B in constant ratio, they will both decay with second order kinetics. At any other ratio of concentrations, at some time either A or B will become the limiting reagent, and the reaction rate will decay exponentially. Thus, condition (14) corresponds to the point of maximum persistence and in this sense, the

stoichiometric endpoint of the titration. We note that the stoichiometric endpoint of this reaction is not defined in the equilibrium sense.

The final mechanism we will consider is



This mechanism is important, for example, if there is an impurity in the system. If in this mechanism,  $k_2 < k_1$ , C will persist at long times and eventually the decay of B will become pseudo-first order. Thus, simultaneous decay of A and B will not be possible. Of course, whether persistent decay of luminescence is perceived or not will depend on the relative rates of the two reactions and the relative concentrations of B and C. A very small concentration of a very slowly reacting "impurity" will clearly have little effect on the titration.

If  $k_2 > k_1$ , reaction with C will be essentially complete before the endpoint is reached, and maximum persistence will be achieved when  $b_0 = a_0 + c_0$ . In this case the variation of intensity around the endpoint will be determined by the value of  $k_1(b_0 - c_0)t$  and be in the variable  $a_0/(b_0 - c_0)$ .

#### Applications

There probably have been times that persistent luminescence at the stoichiometric equivalence point of a gas-phase reaction has been experimentally observed and perhaps even reported in the literature. To the author's knowledge, however, the physical basis and general utility of this phenomenon has not been discussed. One case in

point involves our own work. A number of years ago we reported on recombination emission in the hydrogen-fluorine reaction.<sup>6</sup> In this experiment H<sub>2</sub> was added to F<sub>2</sub> that had been partially dissociated in an electric discharge. A downstream photodetector recorded visible luminescence from highly excited vibrational levels of HF. This luminescence was exceedingly sharply peaked as a function of H<sub>2</sub> addition (varying by three orders of magnitude with a 10% change in H<sub>2</sub> flow). Since added H<sub>2</sub> almost instantaneously converts F atoms into H atoms in this experiment (after undissociated F<sub>2</sub> is removed), the experiments actually involves varying the initial H to F ratio of the flow. The following two mechanisms were proposed to explain the formation of highly excited HF in these experiments:

- A) direct combination of H and F atoms into high vibrational levels of HF, and
- B) recombination of H atoms to form high vibrational levels of H<sub>2</sub>, followed by vibrational energy transfer to HF.

No explanation was offered for the sharply peaked nature of the luminescence in the original report. The present work, not only provides such an explanation, but also allows a choice to be made between the above two mechanisms. Mechanism B, involving only a single consumed reagent (H atoms), would not show a transition from pseudo-first order to second order kinetics. Although it may be occurring in the system, it can not be responsible for the sharply peaked nature of the downstream emission. In mechanism A, however, as F atoms are converted into H atoms, a point is reached where they are at equal concentration and thus their decay is second order in concentration of the atoms. (Actually, third order overall, since the atomic combination reaction requires a third body to remove energy and stabilize HF below its dissociation limit.)

### Conclusion

It appears from these analyses, that in many reactions that produce light with high efficiency, persistent luminescence might be observed. The point of maximum persistence of luminescence will often be at the stoichiometric equivalence point of the reaction, while variation of light intensity around this point may provide important information about the mechanism and kinetics of the reaction system being studied. Care must be taken that wall loss of active species is negligible when analyzing these systems.

### Acknowledgment

The author would like to thank Dr. A. Fontijn for several helpful conversations dealing with this work.

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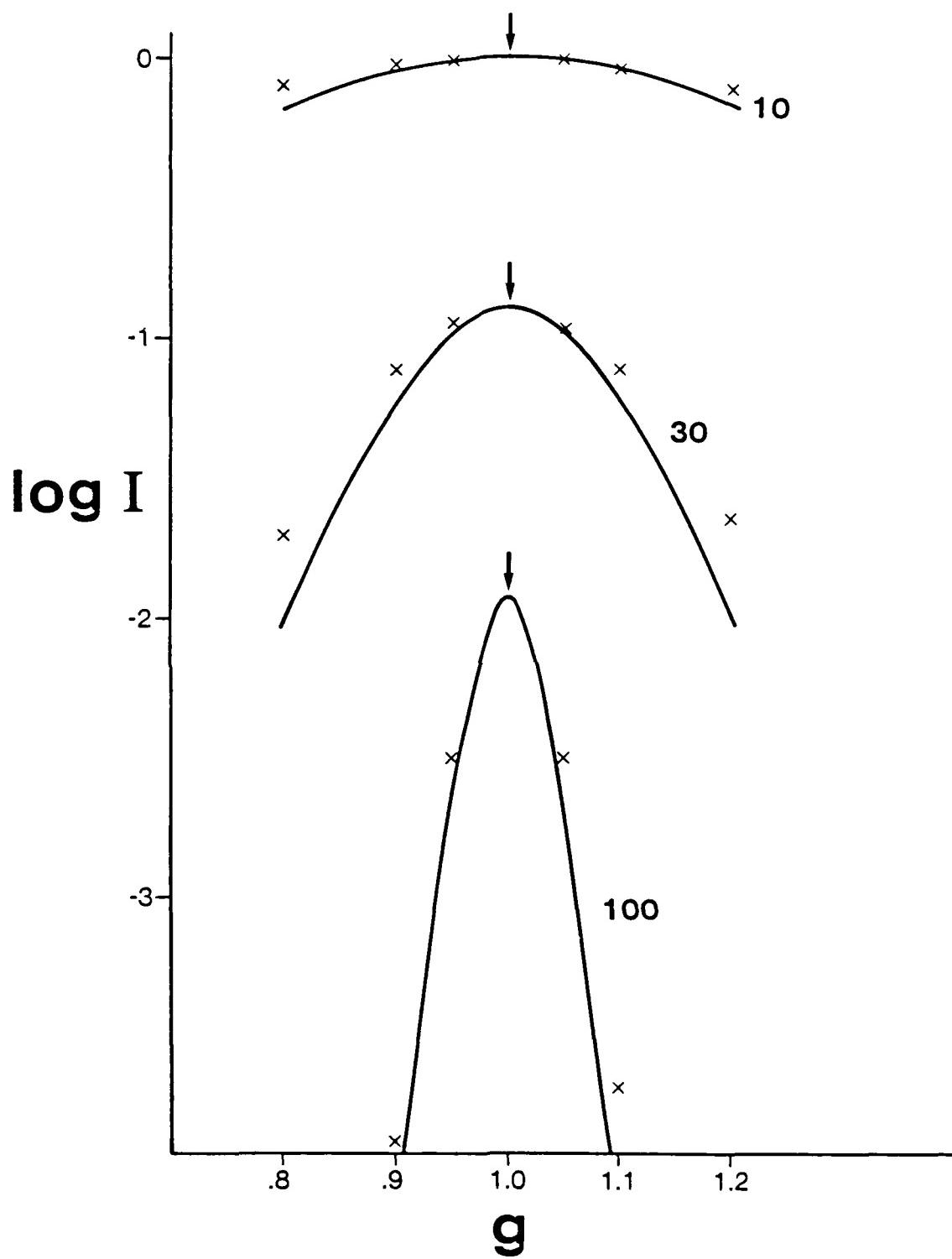


Figure 1. Chemiluminescent intensity as a function of stoichiometric ratio,  $g = a_0/b_0$ , for different values of  $b_0 k_1 t$ . Curves: for an elementary reaction. Crosses: for a two-step series reaction with  $k_1 = k_2$ .

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